

Comment on “Adsorption of Polyelectrolyte onto a Colloid of Opposite Charge”

In a recent Letter, Gurovitch and Sens [1] studied the adsorption of a weakly charged polyelectrolyte chain onto an oppositely charged colloidal particle. By using a variational technique they found that the colloidal particle can adsorb a polymer of higher charge than its own, and thus be “overcharged.” I argue that the observed overcharging by a factor of 16/5 is indeed an artifact of the approximations involved in the study. Moreover, I show that the existence of overcharging for a pointlike colloidal particle depends crucially on the choice of the trial wave function, contrary to their claim.

To study the adsorption, they use a restricted class of trial wave functions $\psi_z(\mathbf{r})$ based on the assumption that the polyelectrolyte is *uniformly* confined in space to a sphere of size $1/z$, and treat z as a variational parameter. A finite value for $1/z$ that minimizes the free energy, called $1/z^*$, would then mean complete adsorption, whereas an infinite $1/z^*$ would imply instabilities in the form of dangling segments stretching away from the core. I use a larger class of trial wave functions

$$\psi^2(\mathbf{r}) = \alpha \psi_z^2(\mathbf{r}) + \frac{(1-\alpha)}{V}, \quad (1)$$

that assumes a fraction α of the chain is confined to a sphere of size $1/z$, while the rest fills up a considerably larger space (of volume V), and treat z and α as parameters. This class of trial functions clearly contains that used in Ref. [1] as a subclass ($\alpha = 1$), and can thus be used to check the robustness of their results.

One can argue why the above choice for the trial wave function is physically more appropriate. The polyelectrolyte can be either adsorbed to the oppositely charged colloid, or stretched out due to self-repulsion. This suggests that an effective two dimensional phase space is more suitable to describe the state of the system. Any configuration of the chain can then effectively be described as a decomposition into various segments, each of which occupying one of the two states, in this simplified picture. The natural question to ask is then the “occupation” ratio of each state, which is determined by minimization of the free energy.

Consider a chain of length N with a fraction f of its monomers being charged, which is adsorbed to a colloid of charge $-Q$. Using $\psi_z(\mathbf{r}) = (z^3/\pi)^{1/2} e^{-zr}$ as in Ref. [1], one obtains the total free energy per unit charge as

$$\frac{E(z, \alpha)}{k_B T} = c_0 a^2 z^2 \alpha - c_1 Q l_b z \alpha + c_2 f N l_b z \alpha^2, \quad (2)$$

in which $l_b = q^2/\epsilon k_B T$ is the Bjerrum length, $a^2 = b^2/f$ where b is the monomer size, and the numerical coefficients are given as $c_0 = 1/6$, $c_1 = 1$, and $c_2 = 5/16$ for the above choice of trial function. Minimizing with respect to z and α yields a “confinement radius” $1/z^* = 3c_0 a^2 / c_1 l_b f Q$, and a “charging fraction”

$$\alpha^* = \left(\frac{c_1}{3c_2} \right) \times \frac{Q}{fN}. \quad (3)$$

Note that within this class of trial functions one always obtains a finite value for $1/z^*$.

The amount of charge that can be adsorbed by the colloid is given by $\alpha^* f N = (c_1/3c_2) Q$, and is equal to $(16/15) Q \simeq 1.07 Q$ for the above choice of trial function, which indeed suggests an overcharging, although considerably smaller than reported in Ref. [1]. However, one can see that this prediction is strongly dependent on the choice of the trial wave function, and thus not robust. For example, a Gaussian wave function of the form $\psi_z(\mathbf{r}) = (z^2/2\pi)^{3/4} e^{-z^2 r^2/4}$ yields the above results with $c_0 = 1/32\sqrt{2}$, $c_1 = 2\sqrt{2}/\sqrt{\pi}$, and $c_2 = 1/\sqrt{\pi}$. In this case, an adsorption of $(2\sqrt{2}/3) Q \simeq 0.943 Q$ charges is predicted, which indicates an “undercharging!”

Finally, I note that a finite size of the colloidal particle (a hard core), and end effects due to finite length of the chain, have recently shown to lead to overcharging [2]. The overcharging is reduced as the size of the particle decreases, and, interestingly, changes into a slight undercharging as it goes to zero [2].

In conclusion, I have shown that a variational approach can not be used to unambiguously determine the degree of charging of a pointlike colloidal particle by an oppositely charged flexible polyelectrolyte.

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